Advances in Building Dye-Sensitized Solar Cells in Ecuador

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Introduction

The fundamental requirement of any solar to electric conversion system is the absorption of a significant part of the incident solar radiation with a consequence utilization of the energy of the photons in an electrical process. There have been three generations of photovoltaic technologies. First generation solar cells build on single crystalline silicon wafers and consist of large area, single p-n junction diodes which can achieve very high efficiency-close to the theoretical efficiency of 33%-although the their production costs are very expensive. Second generation solar cells, represented by thin-film devices based on cadmium telluride (CdTe), copper, indium gallium selenide (CIGS), amorphous silicon and micromorphous silicon, require lower energy and production costs. Unfortunately, they suffer from much reduced energy conversion efficiencies compared to the first generation compared to the first generation because of the defects inherent in the lower-quality processing methods. Third generation solar cell technologies aim to increase the efficiency of the second generation solar cells while maintaining low production costs.

Band gap

A photon´s energy E is inversely proportional to its wavelength λ according to

$$E = h\nu = hc/\lambda \quad (1)$$

Where h is Planck´s constant and c the speed of light. If the energy exceeds the band gap of the semiconductor, the photon can be absorbed and an electron will be excited from the valence band to the conduction band. Electrons in the conduction band can move, which allows for electric current. The difference between the photon energy and the band gap will end up as heat. However, it has been reported that a high energy photon can give a rise to multiple electron-hole pairs in certain materials, and this could be possibly be used to reduce heat loss in solar cells

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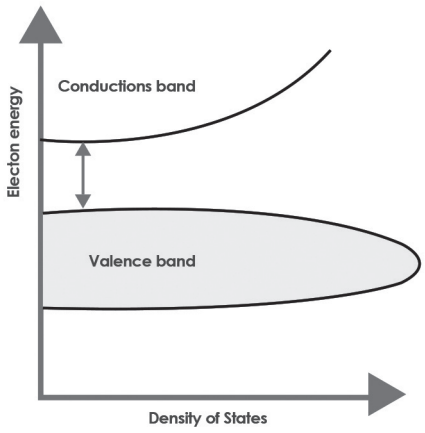
Figure 1
The band gap is the difference in energy between
the valence band and the conduction band



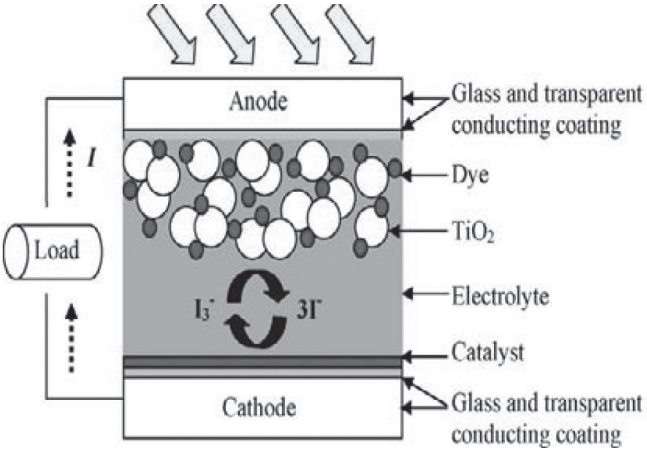
Dye-sensitized solar cell

A dye-sensitized solar cells (DSSC) is a device to change light into electric energy by light sensitization established on wide energy-band semiconductor used as electrode for cells due to their high photochemical stability. However, this type of semiconductor does not have the ability to absorb visible light. Thus, photo sensitizers such as dye particles are added to the material to absorb visible light. DSSCs are of great interest, since O'Regan and Gratzel introduced ruthenium-based complexes such as N3, N719 and black dye, small band gap energy materials have been the preferred materials for the dye due to their high electrochemical activity and have shown solar to electricity energy conversion efficiency of 11%. Because of the photons´ energy cannot be absorbed, if it is smaller than the material´s band gap energy, the sensitizer needs to be stable for over 108 times redox reactions for long lifetime cell. However, the costs of chemical synthetics such as the ruthenium-based complexes restrict their large-scale applications in solar cells. Moreover, the synthesis process of these complexes is very complicated and expensive, stimulating the search for alternatives. Indigenous dyes are environmentally friendly and inexpensive alternative to synthetic dyes. Several natural dyes (chlorophyll, carotene, cyanin, tannin, etc.) have been utilized as sensitizers in DSSCs, however conversion efficiencies are still low. Consequently,, in this contribution, natural dyes from Ecuador were selected as potential sources of stable sensitizers for DSSCs assembly.

A typical DSSC cell structure and its operational principles are shown in Figure 1. It consists of two transparent conducting oxide (TCO), glass substrate coated with a thin layer of interconnected, mesoporous semiconducting nanocrystalline TiO2 covered with dye solution, an electrolyte containing a reductions-oxidation couple e.g. I-/I3-and a catalyst coated counter-electrode, which is usually fabricated with Pt. Light enters the transparent substrate and gets absorbed by the dye molecule adsorbed onto the semiconductor-TiO2-through TCO into the

load. Once the electron is excited, the liquid electrolyte will be oxidized into oxidation state and transfer another electron into the dye electron vacancy to regenerate the dye particle and reduce the possibility of electron recapturing by the oxidized sensitizer. The liquid electrolyte is reduced back to its original form when it accepts electron from the light conductive counter electrode, usually Pt. Finally, the counter electrode regenerates by accepting the electrons from the electric load. Thus, the whole operation process becomes a cycle with zero net chemical change theoretically. Consequently, each inter-media contact is the most important aspect in improving the efficiency and minimizing the energy loss during carrier transfer.

Figure 2
Dye-sensitized solar cell structure



Basic design of A DssC

Transparent Conductive Oxide (TCO)

TCO is a wide bandgap semiconductor that consist of high concentration of free electrons, high transparency, low sheet resistance and good electrical conductivity, the most common ones are: Tin doped Indium Oxide (ITO), Fluorine doped Tin Oxide (FTO) and Aluminum doped Zinc Oxide (AZO). In general the substrates can be made from microscope cover glass, quartz and ITO cover glass, the surface area is approximately 4 cm^2. The cover glass have a thickness of less than 100 um, the other two types are around 300 to 500 μm thick. The ITO glass has a layer of 700 μm of ITO with 7 Ω sheet resistance on one side, whereas the other two have plain substrates with no thin film pre-deposited. A substrate textured layer can be deposited on glass substrates well cleaned before deposition using: a radio frequency (RF) magnetron sputter, similar to physical vapour deposition (PVD), reactive ion etcher (RIE), a combination of physical and chemical etchings. Spin coating is also used when depositing liquid materials, the deposited film thickness is mainly controlled by the spinning speed of the equipment and the viscosity of the material. After deposition annealing, at 450° C for 30 minutes for improving the electrical characteristics of the TCO film (7.8.9).

TiO2 semiconductor

The most commonly used wide band gap semiconductor in DSSC is TiO2. The efficiency of the DSSC depends on the properties of the nanostructured TiO2 electrode, which is used for light absorption and electron transfer. However, due to the fact that the material is a wide band gap semiconductor, shorter wavelength-in the UV range-is required for electron excitation. Therefore, light sensitive dye material is used to coat the semiconductor material for electron excitations within visible wavelength range. The properties of the TiO2 film and the performance of the cell are related to each other. For example, the internal surface area of the film determines the dye uptake, the pore size distribution affects the ion diffusion, the particle size distribution determines the optical properties, and the electron percolation depends on the interconnection of the TiO2 particles.

Investigations on the preparation of nanostructured TiO2 include: colloidal deposition, sputter deposition, sol-gel technique, spray pyrolysis and pressing technique. In this research the first deposition method has been adopted since about 7% conversion efficiency has already achieved by other researchers. Another method is the preparation of nanotubes or nanowires TiO2 nanocrystals with nanorods perpendicular to the substrate by sol-gel technique, this could offer desired directionality for the electron transport in the TiO2 electrode, which could result in a faster photoresponse and higher electron collection efficiencies. However, the main drawback for this method is the toxic solvents.

Sensitizer dye

The purpose of the dye is to absorb as much light as possible and inject the photo-exited electrons into the conduction band of the semiconductor and it supposes to function in a wide thermal range and maintain photo stability for long-term use. To achieve a high light to energy conversion efficiency in the DSSC, the properties of the dye molecule adsorbed on the semiconductor particle surface are essential. For example, the energy of the exited state of the molecule should be about 1.35 eV above the electronic ground state, the exited state of the absorbed dye molecule should be only slightly above the conduction band edge of the TiO2, also the ground state of the molecule should be only slightly below the redox potential of the electrolyte and the kinetics of electron injection from the exited state to the condition band of the semiconductor should be fast enough to outrun competing unwanted relaxation and reaction pathways. In addition, the adsorbed molecule should be stable enough at the semiconductor electrolyte interface to sustain for several years.

Electrolyte

The purpose of electrolyte is to donate electrons to oxidized sensitizer to prevent the excited electrons recaptured by the sensitizer. It has to be a transparent material that allows the light to go through and has good conductivity and fast redox reaction. Liquid Iodide/ Tri-iodide is the most commonly used electrolyte for DSSC. The main problem is that liquid electrolyte often causes leakage and degrades very fast photochemically resulting in short

lifetime for the cell. Solid state electrolyte has been investigated. However it was discovered that it may suffer from poor transparency, which is one of the most important conditions required as electrolyte for DSSC. Consequently, development of quasi-solid state electrolyte such as gel may be the solution in order to provide DSSC cell with better stability another attempt would be to explore clays. The performance and stability of the DSSC can be enhanced to some extent by adding tetrabutylammoniumhydroxide (TBAOH), which converts the light absorbing I3-complexes into olorless IO-ions, which are reduced to I-and OH-ant the counter electrode. The use of TBAOH. It was reported that methoxypropionitrile as potential alternative candidate for the commercial DSSCs.

Counter electrode

The counter electrode needs to provide high conductivity to complete the redox reaction, along with the liquid electrolyte, in a very short time for lifetime stability and preventing the electron recapture. The most common used is Pt, Iodine is chemisorbed on Pt surface, and this process reduces the high activation energy needed to break the I-I bond. Pt has high electron mobility that can regenerate the electrolyte immediately and it has high stability against electrolyte´s corrosives characteristics. For that reason here Pt was selected as counter electrode. Other cathodic materials that have been used are graphite, activated carbon, carbon nanotubes, polypyrrole and carbon-black (amorphous carbon stainless steel).

Cell assembly

Both electrodes, one with TiO2 deposition and the other with Pt coating, should be cleaned in ethanol, dried and staked together face to face and prepared for assembling. Two pieces of transparent spacers with approximately 60μm thick are placed between the substrate to isolate the working space and prevent short circuit between the positive and negative contact pads when the liquid electrolyte is injected. The assembled sample is heated at 80oC for about 15 min to soften so that the top substrate anode, and the bottom substrate cathode can firmly attach together, between the spacers is left small channels for filling the cell with electrolyte, for sealing the cell DuPont Surlyn has been used. Once the cell is properly assembled, the liquid electrolyte is injected into the channels, about 100 μL, after the electrolyte dries out solar cell performance can be tested.

Testing the DSSC

The performance-efficiency and I-V curve-of solar cell depends on the spectral distribution (Wm-2μm-1) and total irradiance power (Wm-2) of illumination, as well as on the environmental conditions e.g. temperature. In order to obtain reliable and comparable data the solar cells are usually measured in research laboratories at standard conditions with solar simulators imitating the standard solar spectrum. In general a Fully Reflective Solar Simulator System is used, which produces high intensity and uniform illumination on a target area with specially designed mirrors that fold the light towards the target, resulting in reduced the

light losses and eliminated the spectral distortion. The light source of 1 SUN (100 mWcm-2) for target size of 25 cm^2 and the type of filter used for the simulation system is Air Mass 1.5G (AM 1.5G). The light source can imitate sun light at different conditions. AM 1.5G provides light surce that is similar to the sun light at the sea level and takes into account of the radiations that are both directly from the sun and reflected back to ground by the sky or the sea. The voltage range for IV measurement is from-1 V to 1 V in steps of 0.1 V, the positive plug is connected to the cathode Pt side, and the negative probe is connected to the TiO2 anode.

Objectives and approach

The primary objective of this study is to investigate the nanofabrication of DSSC using natural pigments to improve the economic and environmental benefit of the DSSC. This include the selection of natural pigments originally from Ecuador, followed by solid-liquid extraction, pH and temperature influence during extraction process, structure and electronic characterization, adsorption of the pigment on TiO2 nanoparticles, DSSC assembly and incident to photon current conversion efficiency for manufacturing DSSC.

Experimental methods

Figure 3
Overall experimental design

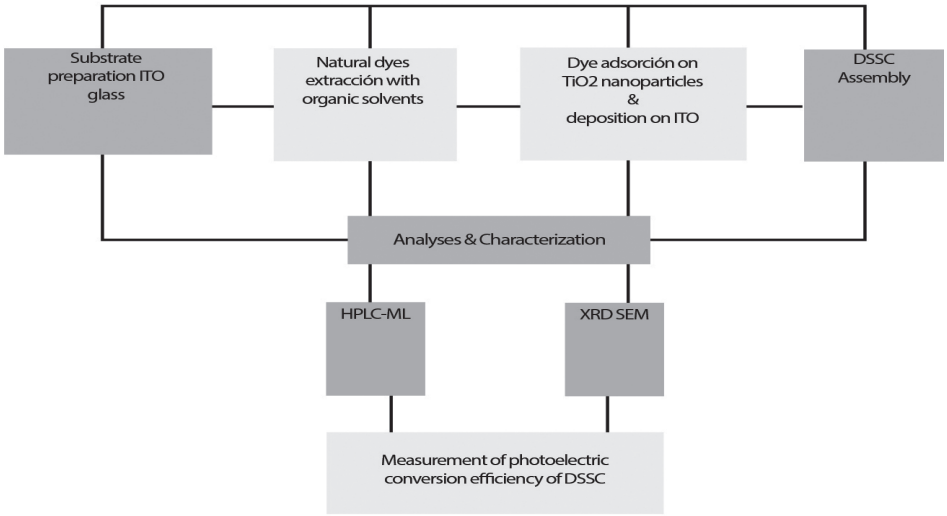


Figure 3 presents a schematic representation of the overall experimental design employed in this study. It represents the flow steps of DSSC nanofabrication and characterization. Of primary concern is the use of natural extracts as sensitizers, which are even more environmentally friendly and low cost alternative to synthetic dyes. Table 1 list the selected natural pigments from plants, seeds and fruits as solar sensitizers. 10g of plant material (lea-

ves, stems) were separately dried (70º C, 24 h) after crushing into fine pieces the materials were immersed into 200 mL of ethanol, and mixing at room temperature to extract its pigments the solid material were filtrated out (0.45 μm), and the filtrates were use as sensitizers. 10 g of fruits were crushed and pooled were extracted with water and filtered before used as sensitizers. TiO_2 films are prepared from dispersions of Degussa P25 TiO_2 in ethanol onto FTO conductive glass (15 Ω/sq), sintered at 450º C, 1 h, which are immersed in one of the natural dyes for 24 h, allowing the natural dye molecules to be adsorbed on the surface on TiO_2 nano-particles. The counter electrode electrolyte is prepared with 0.05 M I_2 and 0.5 M LiI and 0.5M of 4-tert-butylpyridine (4-TBP) mixed with acetonitrile. The counter electrode consist a transparent Pt film on its conductive glass surface. Two pieces of spacers are placed between the substrates at the top and the bottom, leaving a channel for electrolyte injection. The adsorbed TiO_2 and Pt counter electrode are assembled into a sealed sandwich-type cell, the liquid electrolyte is then injected from the bottom of the cell until the whole space is filled. Genesys 5 UV-Vis spectrometer was used for absorption studies. The chemical structure of the most promising dyes will be determined using a HPLC, Waters Separations Module 2695 and MS, Waters Micromass Quattro Ultima The photoelectrochemical parameters of the prepared DSSC will be measured from current-voltage curves obtained under a 91160 Newport/Oriel simulated solar radiation (AM 1.5; 100mW cm^2). The measured results will be plotted in an I-V curve, from which the information of open circuit voltage Voc (V), short-circuit current density Jsc (mA/cm^2), fill factor (FF) and conversion efficiency η % will be determined.

Table 1
Selected natural organic dyes of Ecuador

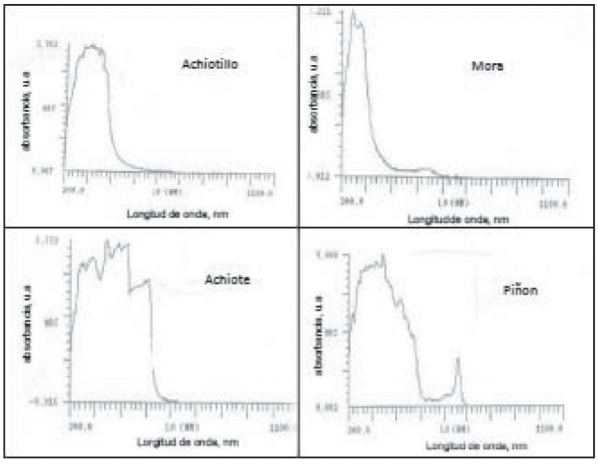
Scientific/common name	Image	λ (nm)
Amaranthus cruentus/ataco		520
chornea ltifolia/achiotillo.		407
*Beta vulgaris/beterraga**		475
Bixia orellana/achiote		460
Ambrozia artemisioides Mill./marco		515
*Rubus robustus C. Presl/mora**		320
*Solanum americanum Mill./mortiño**		610
Iresine herbstii Hook/escancel		627
Jatropha curcas L./piñon		418
Baccharis latifolia/chilco		563

* Extracted with water

Results and discussions

Progress to date: table 1 shows some plants, leaves, flowers, and fruits, which exhibit various colors and contain several pigments that can be easily extracted and used in DSSCs. It also shows the values of maximum absorptivity λmax of the dyes extracted with ethanol and water. Fig. 4 shows the representative UV-Vis absorption spectra for the ethanol extracts of achiotillo, achiote, mora and piñon exhibit an absorption peak of 407 nm, 460 nm 320 nm, and 418 nm, respectively. λmax values higher than 600 nm e.g. mortiño an escancel suggest that these natural plant pigments can be used as sensitizers with the potential to improve the economic and environmental benefit of the DSSC. Several natural dyes have been employed as sensitizers in DSSCs, such as chlorophyll (green), anthocyanin (purple-red), cyanin, carotene, tannin, and others but, the efficiencies η of solar energy conversion are rather low. For example, an η value of 0.66% was obtained using red Sicilian orange juice, 0.56% using cyanine from balcakberries, using Rose Bengal dye as sensitizer resulted an η value of 2.7%. Furthermore, it has reported that structural modification of coumarin and used the coumarin derivation dye as sensitizer in their DSSC, which provided an η value of 7.6%, while dye solar cell sensitized with the betalian and betaxanthin pigments reported η values of 14% and 8%, respectively, the efficiencies, natural plant pigments serving as sensitizers have the potential to improve the economic and environmental the benefits. This suggest that more work need to be done, in order to optimize the performance of DSSCs. Thus, a collaborative effort between ESPOL and UTPL has been established for exploring the effect of other solvents used to extract natural dyes, such as chloroform, ethyl acetate, n-butanol and petroleum ether is currently explored, as well as the temperature and pH. In addition, chemical and electronic dyes determination to achieve more efficient incident photon to electron conversion, and to explore other dye depositions methods on TiO2 nanoparticles, that may allow maximizing energy conversion efficiency η

Figure 4
UV-vis absorption spectra of natural dyes of Ecuador



Conclusions

This ongoing project was designed to provide information regarding the nanofabrication of DSSC and the use of natural dyes native from Ecuador as sensitizer in a DSSC. In principle, 12 natural dyes were extracted with ethanol or water and characterized by UV-vis absorption spectra and maximum wavelength, the values suggest the potential to use the dyes as sensitizers to prepare DSSCs. Future work will be directed at optimizing the extraction method using other solvents and explore the influence of the temperature and pH, the molecular and electronic structure of dyes, and characterize the sensitizer for DSSC, in order to maximize energy conversion efficiency because of their low cost production and environmental friendly.

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